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FORMATION OF POROUS SURFACE LAYERS  
IN REACTION BONDED SILICON NITRIDE  
DURING PROCESSING

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## FORMATION OF POROUS SURFACE LAYERS IN REACTION

## BONDED SILICON NITRIDE DURING PROCESSING

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## SUMMARY

Microstructural examination of reaction bonded silicon nitride (RBSN) has shown that there is often a region adjacent to the as-nitrided surfaces that is even more porous than the interior of this already quite porous material. Because this layer of large porosity is considered detrimental to both the strength and oxidation resistance of RBSN, a study was undertaken to determine if its formation could be prevented during processing.

All test bars studied were made from a single batch of Si powder which was milled for 4 hours in heptane in a vibratory mill using high density alumina cylinders as the grinding media. After air drying the powder, bars were compacted in a single acting die and hydropressed.

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Sintering and nitriding were performed in furnaces with high-purity alumina tubes using high purity bottled gases. Both processes were done under three different conditions: 1. the bars were exposed directly to the gas flow 2. the bars were packed in Si powder 3. the bars were packed in  $\text{Si}_3\text{N}_4$  powder.

Bars were sintered in He with hold times at  $1200^\circ\text{C}$  of from 0 to 256 hours. The porous surface layer was formed on the top surface of most bars exposed directly to the gas flow. It did not form on bars protected by either powder. However, those bars sintered for very long times formed a network of large bonded Si particles and interconnected porosity throughout the bar. Weight losses during sintering corresponded to evaporation of  $\text{SiO}$ .

Nitriding was done at a maximum temperature of  $1400^\circ\text{C}$  in an atmosphere of  $\text{N}_2$ -4%  $\text{N}_2$ . The same nitriding cycle was used in all cases. Bars nitrided in  $\text{Si}_3\text{N}_4$  powder or exposed to the gas flow developed the layer of large porosity. Bars packed in Si powder did not develop an unusually porous surface layer. It is suggested that the direct relationship between  $\alpha/\beta$  ratio and oxygen content could be explained by a sheath of amorphous silica on the  $\alpha$ - $\text{Si}_3\text{N}_4$  crystallites.

The presence or absence of the surface layer did not seem to affect the measured strengths. Bars nitrided exposed to the gas flow averaged 250 MPa and those packed in  $\text{Si}_3\text{N}_4$  272 MPa. The failure initiating flaws were generally large subsurface pores, much larger than the surrounding porosity. The bars nitrided in Si powder had much lower measured strength (171 MPa). These bars failed from surface damage caused during removal of the bars from the Si powder which had nitrided into a hard cake.

The layer of surface porosity may be more important to the oxidation resistance of RBSN than to the strength at the present state-of-the-art. Strength improvement is dependent on elimination of the few very large subsurface pores.

## INTRODUCTION

The bend strength of reaction bonded silicon nitride (RBSN), like that of other ceramic materials, is extremely sensitive to surface and near-surface irregularities such as pores and inclusions. Microstructural examination of RBSN test bars after nitriding has shown that the region near the surface often has larger porosity than the interior of the bars. This layer, 100-200  $\mu\text{m}$  in depth, has been observed in both laboratory and commercial samples of RBSN (Fig. 1). Much of the porosity is in the 2  $\mu\text{m}$  - 10  $\mu\text{m}$  size range, however, an occasional pore as large as 50  $\mu\text{m}$  also is present. In the balance of this paper, any reference to a porous surface may be understood to refer to a surface layer in which the size of the pores exceeds average pore size in an RBSN sample.

In addition to its deleterious effect on mechanical properties, this porous surface layer also significantly reduces the oxidation resistance of RBSN<sup>1</sup>. Dense  $\text{Si}_3\text{N}_4$  derives its oxidation protection from the formation of a passive oxide layer on the surface. However, the large amount of interconnected porosity and resultant large surface area prevent such an oxide layer from effectively protecting RBSN.

Removing the excessively porous surface layer by machining is not economical for complex shapes and defeats a major advantage of RBSN, i.e. the potential for near-net shape component manufacturing. Some efforts have been made to overcome this difficulty by application of surface coatings or infiltration of the specimens with materials that could be chemically reacted to fill the voids with  $\text{Si}_3\text{N}_4$  or other compounds.<sup>1,2</sup> Neither method has been completely successful. Prevention of the formation of this layer of large porosity during the initial sintering and reaction bonding may be a more practical approach to the problem.

This study was undertaken to determine the manner in which different processing steps effect the formation of near-surface porosity and whether it's formation could be prevented during processing. Bars made from a single batch of wet milled Si powder were sintered and nitrided either directly exposed to the furnace atmosphere or packed in either Si or  $\text{Si}_3\text{N}_4$  powder. Evaluation included light and scanning electron microscopy, bend testing, chemical analysis and x-ray diffraction.

## MATERIALS AND PROCEDURE

### Silicon Preparation

The silicon powder for this study was prepared by wet milling as-received -325 mesh Si powder\* in a vibratory mill\*\*. Previous work<sup>3</sup> had shown that bars made from powder milled to a finer particle size nitrided more completely and were stronger than bars made from as-received powder.

The vibratory mill (Fig. 2) employed consisted of a vertical annular milling chamber attached directly to a driving mechanism which, because of eccentric weights, produced three-dimensional high-frequency vibrations. The grinding media were 91 kg of 1.3 cm diameter, 1.3 cm long high density alumina cylinders. A charge of 840g of Si powder and 8 liters of heptane was milled for 4 hours under an Ar cover gas.

After milling for 4 hours the resultant slurry was drained from the chamber and air dried to a friable cake. The caked powder was forced through a 70-mesh stainless steel screen to facilitate pressing.

Test bars were made by cold compacting approximately 3.2g of powder with no binder into bars 76 mm x 9.5 mm x 3 mm in a uniaxial single acting die at 170 MPA. The bars were quite fragile as pressed. The green strength was increased somewhat by cold isostatic pressing at 275 MPA.

### Sintering and Nitriding

The sintering cycle consisted of a 4 hour linear heat-up to 1200°C, a hold at 1200° for times of 0 to 256 hours, followed by an in-furnace cool-down taking approximately 24 hours. An ultra high purity He bottled gas source provided a sintering atmosphere with moisture and oxygen contents both below 5 ppm. The rate of He flow through the furnace during sintering was 470  $\text{cm}^3/\text{min}$ .

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\*\* Sweco, Inc, Los Angeles, California

A nitriding cycle developed by Mangels<sup>4</sup> which had a maximum temperature of 1400°C was used for all nitriding. This cycle is shown in Figure 3. Previous unpublished work of the authors had shown that this cycle is satisfactory for nitridation of both fine and coarse silicon powders. Both the N<sub>2</sub> and H<sub>2</sub> used to make the N<sub>2</sub>/4 H<sub>2</sub> nitriding atmosphere were ultra high purity. The gases were run through purifiers prior to entry into the furnace to remove O<sub>2</sub> and H<sub>2</sub>O to levels of 1-2ppm and 1 ppm, respectively. Flow of the N<sub>2</sub>/4 percent H<sub>2</sub> nitriding atmosphere through the furnace was maintained at 10 cm<sup>3</sup>/min by a flowmeter with the outlet gas going through a bubbler to give a 2.3 MPa backpressure.

The furnaces used for sintering and nitriding had 9 cm diameter x 152 cm long high purity alumina tubes heated by silicon carbide heating elements.

Specimens were either placed on RBSN cylinders or balls or surrounded by lightly packed Si or Si<sub>3</sub>N<sub>4</sub> powder, in a high purity Al<sub>2</sub>O<sub>3</sub> boat on an Al<sub>2</sub>O<sub>3</sub> "D"-shaped tray in the central 15 cm of a furnace tube where the temperature variation could be held within + 2°C. After the furnace was sealed and leak checked, the system was purged for at least 1 hour with the gas to be used. Then the desired cycle, controlled by a curve following programmer was run.

### Evaluation

Bar dimensions and weights were measured after each processing step: compacting, sintering, nitriding. Density was calculated from these measurements. Strengths of bars at room temperature were determined in both the sintered and nitrided conditions by 1/3 point 4-point modulus of rupture tests. Bars were sectioned for polishing (Fig. 4) so that an interior portion received the same metallographic treatment as the sintered or nitrided surface to insure that surface-to-center variations were real, and not polishing artifacts. X-ray diffraction analysis of the phases present in the nitrided bars was made using the method developed by Gazzara and Messier<sup>5</sup> to determine the amount of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and residual Si. Oxygen and nitrogen contents were determined by inert gas fusion and carbon by combustion-chromatographic analysis.

## RESULTS AND DISCUSSION

### Powder Characteristics

The wet vibratory milling process considerably reduced both average particle size and the maximum size Si particle as may be seen in Figure 5. Milling for 4 hours increased the powder surface area from 3 m<sup>2</sup>/g to 7.4 m<sup>2</sup>/g. A large fraction of the milled powder was submicron in size and nearly all the powder particles were below 10  $\mu$ m. This is in contrast to Si powder prepared by dry attrition milling<sup>3</sup> in which numerous large silicon particles were retained even at much higher surface areas (finer average size).

Oxygen, carbon and aluminum contents of the Si powder all increased with milling time. Iron initially increased, and then remained essentially constant. See Table I.

## SINTERING

Data for bars sintered under the three conditions are listed in Table II and discussed below. Three different types of evidence of sintering were noted: development of strength, decrease in sample dimensions, and neck formation between Si particles. All of three processes were time-dependent as was weight loss.

Upon SEM examination of fracture surfaces of bars sintered in He with a 4 hour hold at 1200°C, it was noted that the morphology near the surface exposed directly to the gas flow was different from that of the rest of the bar. As can be seen in Figure 6(a), substantial neck formation occurred, along with the elimination of most of the very small particles resulting in a top surface layer with a network of large bonded interconnected Si particles and interconnected porosity. The lower surface, not exposed directly to the gas flow, and the interior of the bar both were unchanged in appearance from that of an unsintered bar (Fig. 6(b)). No necks were visible and the Si particles were more angular and generally smaller than at the exposed surface.

Greskovich and Rosolowski<sup>6</sup> have determined that the development of the necked microstructure seen in Figure 6(a) in Si is caused primarily by vapor phase transport, although they did not definitely identify the vapor species.

Bars sintered exposed to He with no hold at 1200°C show no evidence of neck formation (Fig. 7); however, there was enough particle bonding to strengthen the bars slightly.

Sintering with a 65 hour hold at temperature resulted in necked structures and large, interconnected porosity through the entire bar (Fig. 8). Light microscopy clearly shows the microstructural difference between bars sintered with no hold time at 1200°C and bars held at 1200°C for 65 hours (Fig. 9(a) and (b)).

The time-dependent nature of the sintering process suggested that the loss of some sintering - retarding species promoted neck formation, leading to the formation of large pores. Increasing weight loss with sintering time indicated that the removal of some species was occurring by evaporation. As discussed below, the weight loss appeared related to evaporation of SiO, a product of the breakdown of the surface SiO<sub>2</sub> layer on the Si powder particles.

In an attempt to inhibit the evaporation of Si (in whatever form) from the surface, bars were sintered packed in either Si or Si<sub>3</sub>N<sub>4</sub> powder. These two powders were chosen to avoid the introduction of contaminants into the system. They also would be expected to sinter very little themselves, allowing removal of bars from the powder bed.

Powder packing retarded formation of the large interconnected porosity at the surface. No evidence of large surface porosity was seen by either light metallographic or SEM examination of bars sintered up to 16 hours in Si<sub>3</sub>N<sub>4</sub> or 4 hours in Si. However, much longer sintering times in Si<sub>3</sub>N<sub>4</sub> produced a uniform network of large interconnected particles and pores throughout the bar as with direct exposure to the flowing He.

Although packing in powder yielded uniform sintered structures, weight loss still occurred at approximately the same rate as in the bars directly exposed to the gas flow. Weight loss in Si<sub>3</sub>N<sub>4</sub> was more rapid initially than after extended sintering.

Noting that oxygen content decreased with time, the change in weight of oxygen of bars packed in  $\text{Si}_3\text{N}_4$  powder was plotted as a function of time in Figure 10. From the line (solid) determined by oxygen loss, the dashed line representing total weight loss was calculated, assuming oxygen was lost as  $\text{SiO}$ . The actual total weight loss (triangles) agrees well with this calculated weight loss.

### Nitrided Specimens

Dimensional changes during nitridation, chemistry, strengths and phases present in nitrided bars are listed in Table III and discussed below.

There was negligible length change in this step for any of the bars. Generally weight gains were greater than 60 percent, indicating nearly complete nitridation. Theoretical weight gain assuming complete nitridation of initially pure Si and no evaporation losses is 66.7 percent. Nitrided densities varied with sintered density, not nitridation conditions. The generally low residual Si content as determined by x-ray diffraction was also indicative of virtually complete nitridation. No  $\text{Si}_2\text{N}_2\text{O}$  was detected in any of the nitrided samples.

Those surfaces exposed directly to the furnace atmosphere during nitridation showed large surface porosity (Fig. 11). As with the sintered bars, it is assumed that the porosity results from evaporation of some species from the near-surface region of the bar. These bars had an oxygen content 15-20 percent higher than would be expected, even assuming no oxygen loss during nitridation. (The bars sintered 256 hours in  $\text{Si}_3\text{N}_4$  had an oxygen content 58 percent greater than expected). Even though ultra-pure gases were supplied to the furnace small amounts of additional oxygen are available as oxygen and water vapor in the nitriding gas, volatile oxides from the furnace tube, oxygen leakage into the furnace, etc. The presence of this oxygen prevents determination of the vapor species leaving the bars.

Large surface porosity was also present in the bars nitrided packed in  $\text{Si}_3\text{N}_4$  powder (Fig. 12). These bars contained up to 190 percent more oxygen than calculated from the oxygen content of the sintered bars. Additional oxygen could come from the  $\text{Si}_3\text{N}_4$  packing powders which had an oxygen content of 1.75 percent. The carbon content of 0.27 percent of the packing powder probably contributed to the high carbon content of these bars.

Except for bars initially sintered in  $\text{Si}_3\text{N}_4$  for 64 hours, bars nitrided packed in Si powder showed no unusual surface porosity (Fig. 13). The Si packing powder could supply Si and  $\text{SiO}$  vapor to suppress volatilization from the bars. Oxygen content of these bars was not (except for those sintered for 256 hours) significantly different from the content calculated from the oxygen content of the sintered bars. The Si packing powder may "getter" the excess oxygen before it reaches the bars.

Possible relations between these oxygen contents and other properties of the materials were considered. It was noted that  $\alpha/\beta$  ratio was directly related to the oxygen content (Fig. 14). In 1972, Wild, et al<sup>7</sup> reported that  $\text{Si}_3\text{N}_4$  with a high  $\alpha/\beta$  ratio contained more oxygen than that with a low  $\alpha/\beta$  ratio. They attributed this to the  $\alpha$  structure being a distortion of the  $\beta$  structure containing oxygen atoms and nitrogen vacancies and having a formula of  $\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$  or  $\text{Si}_{12}\text{N}_{15}\text{O}_{0.5}$ . In 1974, Edwards, et al<sup>8</sup> reported measurements of  $\alpha$ - $\text{Si}_3\text{N}_4$  with little or no oxygen content. Two years later,



Campos-Loriz and Riley<sup>9</sup> suggested that the main role of oxygen is as a Si carrier. It is now generally accepted that  $\alpha$  is not an oxynitride, but there appears to be no consensus on the relationship between  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and oxygen, if any.

Evans and Sharp reported<sup>10</sup> transmission electron microscope studies of RBSN. They found coarse  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> whiskers surrounded by a thin sheath of what appeared to be amorphous silica. It has been proposed by Elias and Lindley<sup>11</sup> that  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> grows in the form of small whiskers by the vapor phase transport of SiO during the reaction bonding process. The diameter of the  $\alpha$  grains in the material produced in this study was estimated by x-ray diffraction techniques to be  $\sim 250\text{\AA}$ .

If each  $\alpha$ -whisker grew with a sheath of amorphous silica, the  $\alpha/\beta$  ratio would be expected to be proportional to the oxygen content. (Some of the total oxygen in the bar would be present combined as other metallic oxides and as surface silica, but this amount should be fairly constant from bar to bar.) Since it is possible to form  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> with little oxygen, a sheath of silica is not necessary to its formation, but is a likely occurrence under normal processing conditions.

From data of this study, it has been estimated that the average thickness of such a silica layer would be on the order of  $10\text{\AA}$ . Very thin amorphous layers are extremely difficult to verify with TEM and little work has been done on RBSN to even differentiate individual  $\alpha$  crystallites.

As shown in Table III, there does not seem to be a relationship between strength of the nitrided bars and sintering conditions,  $\alpha/\beta$  ratio, or the presence or absence of excess surface porosity after sintering. In general, the strongest bars, with an overall average strength of 272 MPa, were those nitrided packed in Si<sub>3</sub>N<sub>4</sub> powder. Most of these bars had a porous surface layer.

Failure initiating flaws were, in most cases, pores as large as  $50\text{ }\mu\text{m}$  just below the surface of the bar (Fig. 15(a)), the formation which is not yet understood. Some large pores at the surface were also noted (Fig. 15(b)). It can be seen in these SEM photos that these pores are much larger than the porosity of the surrounding matrix. These results with wet milled Si contrast with the previous work<sup>12</sup> with dry milling. In that work, fracture often originated from the residual Si particles which were too large to nitride completely. The absence of Si particles as fracture origins in this study may be taken as an indication of the more complete size reduction of Si powder size in the vibratory wet milling process.

The bars packed in Si for nitridation were difficult to remove from the Si powder which had nitrided into a hard cake. Surface damage incurred during removal may account for the relatively low strengths of bars nitrided in Si. The most frequent fracture origins for these bars were surface irregularities.

## CONCLUSIONS

Microstructural examination of reaction bonded silicon nitride (RBSN) has shown that there is often a region adjacent to the as-nitrided surfaces that is even more porous than the interior of this already quite porous material. Because this layer of large porosity is considered detrimental to both the strength and oxidation resistance of RBSN, a study was undertaken to determine if its formation could be prevented during processing.

Sintering

- Formation of porosity proceeds from the surface inward, apparently promoted by the removal of a sintering - retarding species.
- Weight loss corresponds to evaporation of SiO.
- Packing in Si or Si<sub>3</sub>N<sub>4</sub> powder retards formation of surface porosity.

Nitridation

- Surface porosity can be prevented by packing in Si powder.
- Strength is limited by large flaws, not the porous surface layer.
- $\alpha/\beta$  ratio is directly proportional to oxygen content perhaps because of the formation of a sheath of amorphous silica on the  $\alpha$  crystallites.

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TABLE I. - CHEMICAL ANALYSIS OF Si POWDER AFTER  
VIBRATORY MILLING

Milling time, hr	O	C	N	Fe	AL	$\bar{S}, \text{m}^2/\text{g}$
	Percent					
As received	0.71	0.04	0.013	0.61	0.125	3.0
1/2	.84	.08	.014	.95	.150	---
1	.95	.08	.014	.92	.159	---
2	1.09	.13	.014	.97	.190	---
3	1.21	.14	.019	.90	.189	---
4	1.31	n.d.	.019	.88	.204	7.4

n.d. not determined.

TABLE 11. - CHARACTERISTICS OF BARS SINTERED AT 1200° C

Condition, time, hr	Δ Percent weight	Δ Percent length	ρ, g/cm <sup>3</sup>	4-Pt bend strength, MPa	Percent O	Percent C	Percent N	Porous surface layer
As compacted exposed to He flow	-----	-----	1.3	< 0.7	1.66	b	0.019	-----
0	0	+0.1	a	a	a	a	a	absent
4	-1.2	-2.7	1.5	48.3	1.80	.14	.025	present
65	-3.5	-4.3	a	a	a	a	a	present
Packed in Si powder								
4	-1.2	-3.2	1.5	53.6	1.62	.11	a	absent
Packed in Si <sub>3</sub> N <sub>4</sub> powder								
1	-1.5	-1.8	1.4	19.0	1.52	.14	.030	absent
4	-1.9	-2.5	1.5	45.2	1.40	.16	.046	absent
16	-1.5	-2.7	1.5	44.9	1.10	.14	.042	absent
64	-3.2	-4.1	1.6	66.2	.50	.14	.025	absent
256	-3.8	-3.9	1.5	62.2	.31	.22	.042	absent

a Not measured.

b Estimated.

TABLE 111. - CHARACTERISTICS OF NITRIDED BARS

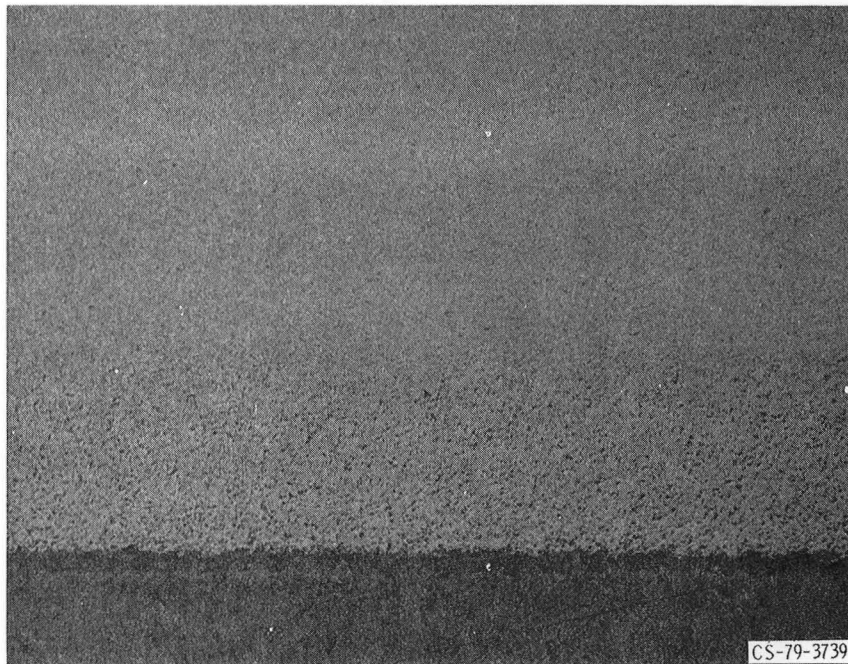
Sinter		Nitride environment	ΔPercent weight	ΔPercent length	ρ, g/cm <sup>3</sup>	Percent O	Percent C	Strength, MPa	Percent α-Si <sub>3</sub> N <sub>4</sub>	Percent β-Si <sub>3</sub> N <sub>4</sub>	Percent Si	α/β	Porous surface layer
Time at 1200° hr	Environ- ment												
a		Si <sub>3</sub> N <sub>4</sub>	60.1	-0.1	2.3	1.12	0.18	243	81	19	n.d. <sup>d</sup>	4.1	present
0	Gas	Gas	62.1	0	2.3	1.32	b	195	83	17	<1	5.0	present
4	Gas	Si <sub>3</sub> N <sub>4</sub>	60.1	0	2.5	1.02	.20	290	81	19	n.d.	4.1	present
65	Gas	Gas	64.2	+1.4	2.4	.50	.21	260	53	47	<1	1.1	present
4	Si	Gas	62.1	-1.1	2.4	1.20	b	248	74	26	<1	2.9	present
		Si <sub>3</sub> N <sub>4</sub>	60.0	-1.2	2.5	1.00	.17	316	79	21	n.d.	3.7	present
1	Si <sub>3</sub> N <sub>4</sub>	Gas	62.1	-1.1	2.3	1.11	.093	229	79	20	1	4.1	present
		Si <sub>3</sub> N <sub>4</sub>	59.7	+1.1	2.3	1.50	.40	288	85	15	<1	5.6	present
		Si	63.9	+1.1	2.3	.97	.078	----- <sup>c</sup>	75	25	<1	3.0	absent
4	Si <sub>3</sub> N <sub>4</sub>	Gas	62.1	0	2.4	.97	.098	235	78	21	1	3.7	present
		Si <sub>3</sub> N <sub>4</sub>	59.7	-1.1	2.4	1.39	.44	263	84	15	1	5.7	present
		Si	62.1	+1.1	2.4	.86	.12	166 <sup>c</sup>	75	24	1	3.2	absent
16	Si <sub>3</sub> N <sub>4</sub>	Gas	62.6	0	2.4	.80	.12	267	76	23	1	3.3	present
		Si <sub>3</sub> N <sub>4</sub>	60.1	-1.1	2.4	1.24	.50	264	81	18	1	4.4	present
		Si	63.5	0	2.4	.73	.098	195 <sup>c</sup>	72	27	1	2.1	absent
64	Si <sub>3</sub> N <sub>4</sub>	Gas	62.6	+1.1	2.5	.36	.12	300	55	44	1	1.2	present
		Si <sub>3</sub> N <sub>4</sub>	60.2	0	2.5	.90	.48	290	59	40	1	1.5	present
		Si	61.2	+1.5	2.5	.32	.080	----- <sup>c</sup>	77	23	<1	3.4	present
256	Si <sub>3</sub> N <sub>4</sub>	Gas	62.5	0	2.5	.30	.18	262	55	44	1	1.3	present
		Si <sub>3</sub> N <sub>4</sub>	59.7	+1.1	2.4	.42	.45	218	53	46	1	1.2	present
		Si	56.9	+1.1	2.4	.28	.068	162 <sup>c</sup>	48	43	9	1.1	absent

a Not sintered.

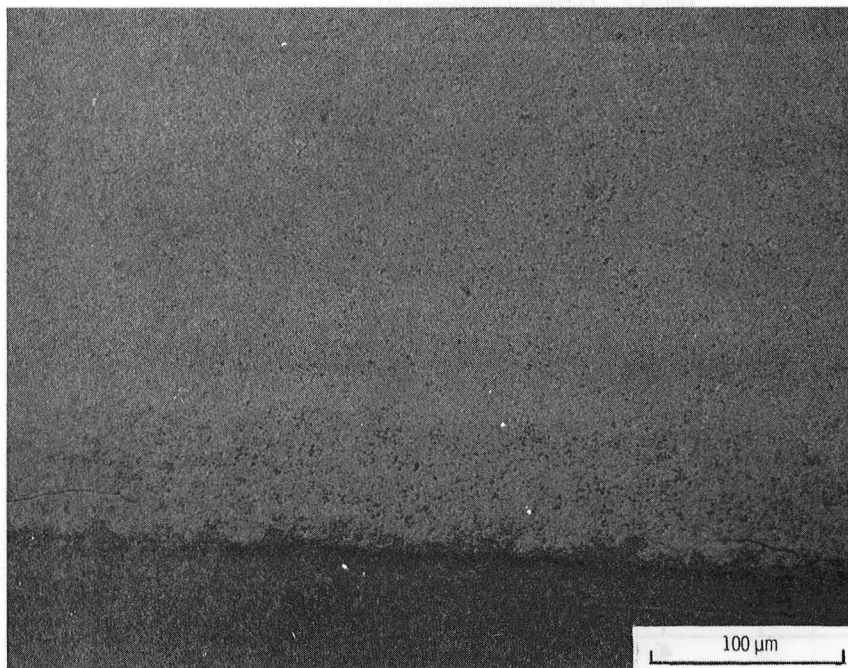
b Not measured.

c Surfaces of bars damaged during removal from Si.

d None detected.



(a) EXPERIMENTAL.



(b) COMMERCIAL RBSN.

Figure 1. - Porous surface layer in RBSN.

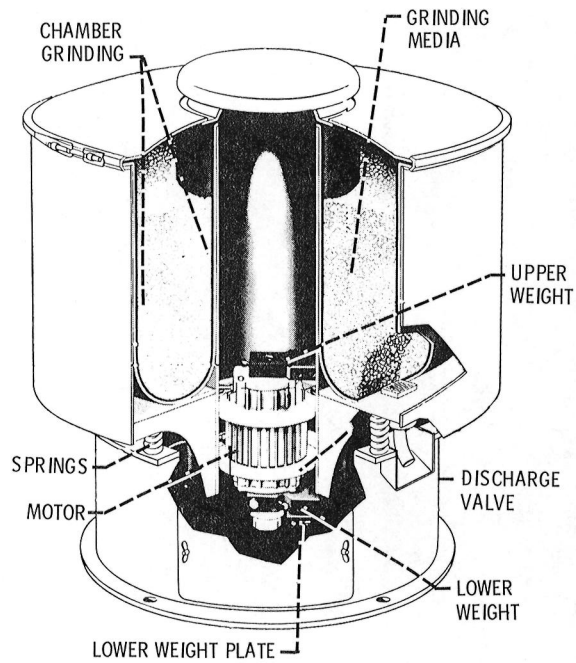


Figure 2. - Cutaway of vibratory mill.

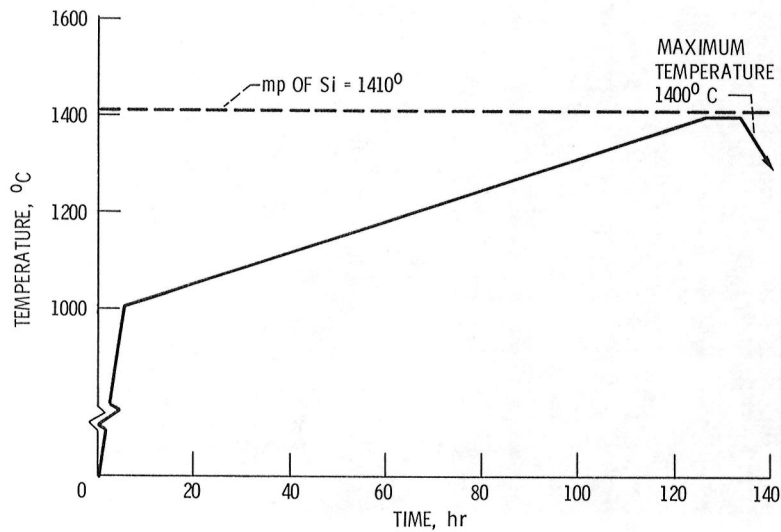
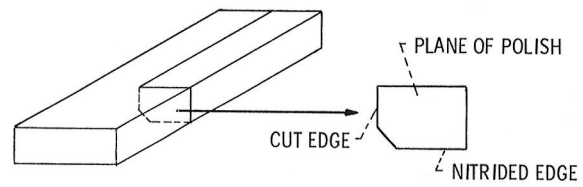
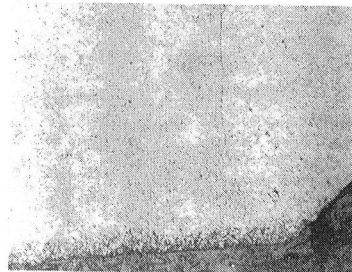


Figure 3. - Nitriding cycle.



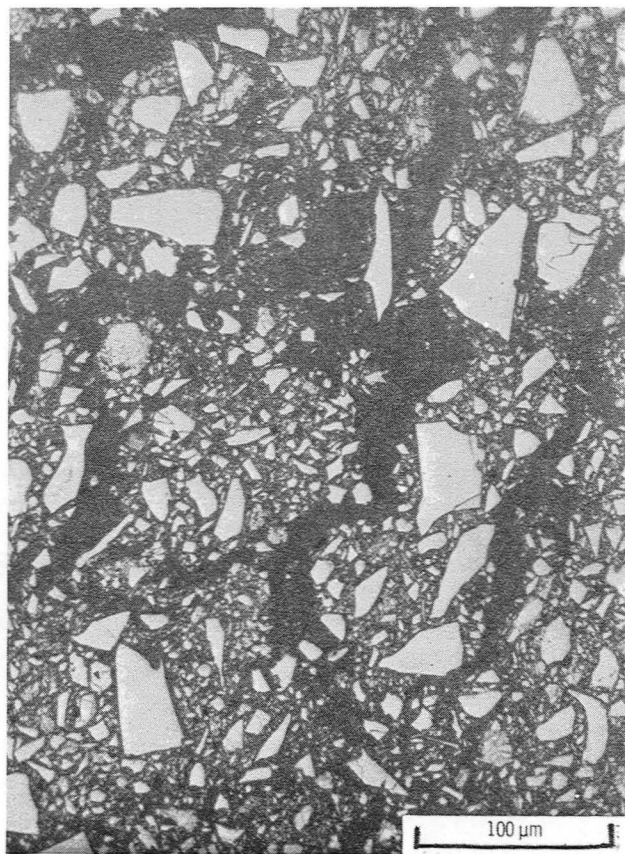
(a) SECTION TO BE POLISHED CUT FROM TEST BAR.



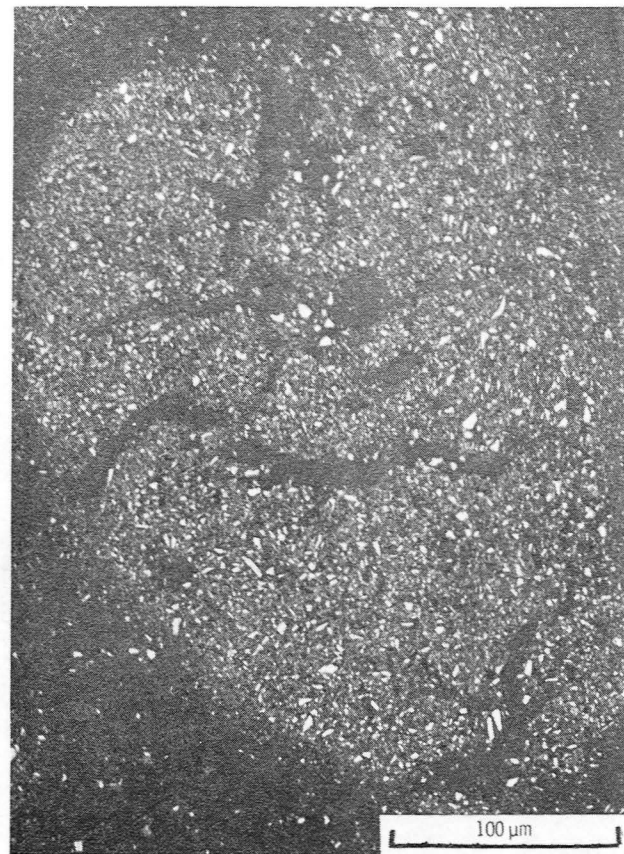
100  $\mu\text{m}$

(b) POLISHED SECTION SHOWING POROSITY AT NITRIDED EDGE, BUT NOT AT CUT (INTERIOR) EDGE

Figure 4. - Test bar.



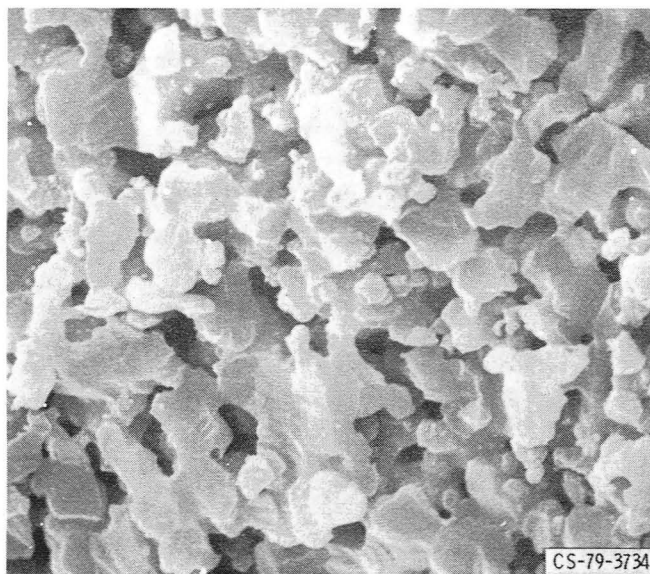
(a) AS-RECEIVED SILICON POWDER.



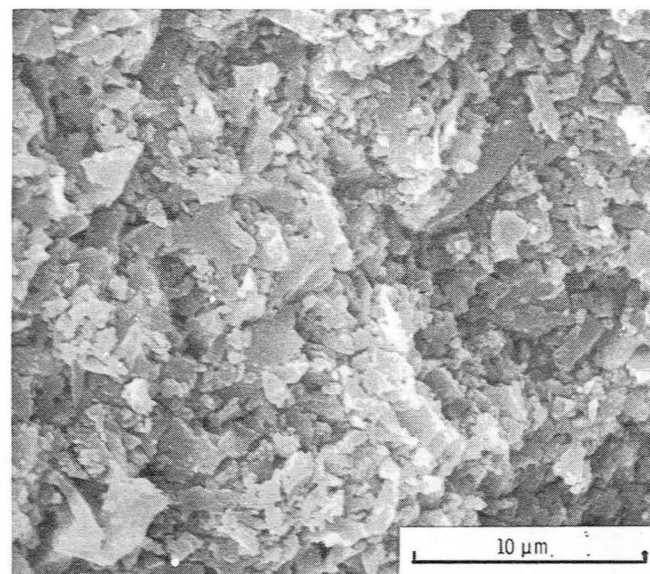
(b) SILICON POWDER VIBRATORY MILLED 4 hours IN HEPTANE.

Figure 5. - Comparison of as-received and milled Si powder.



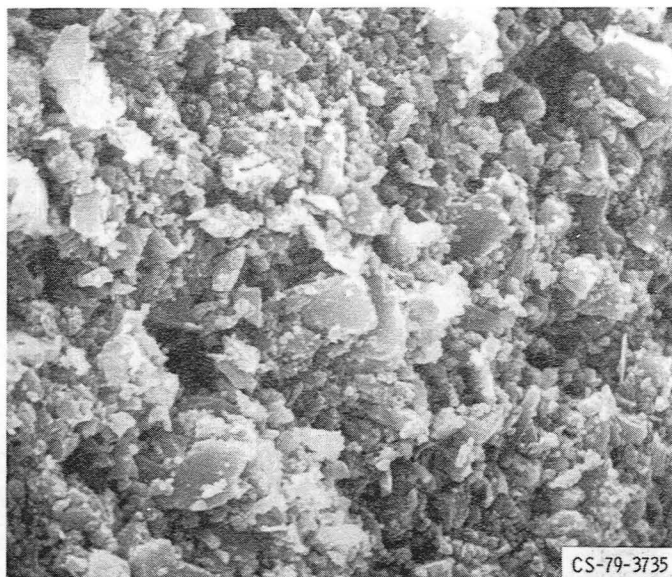


(a) NEAR SURFACE EXPOSED TO GAS FLOW.

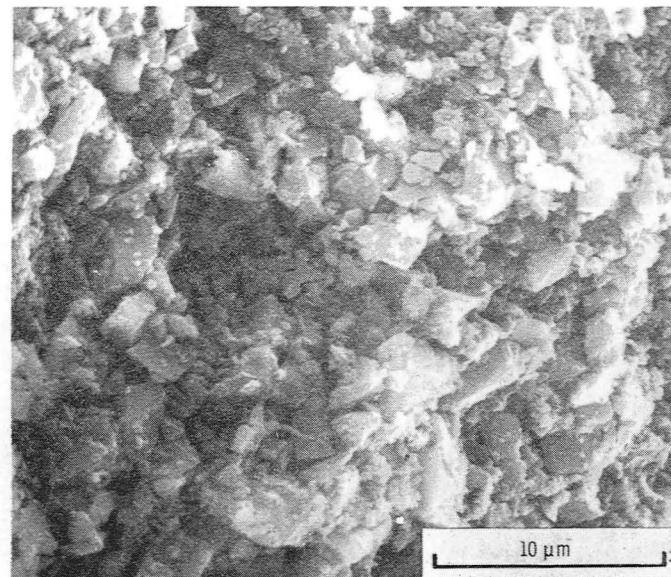


(b) INTERIOR OF BAR.

Figure 6. - SEM photographs of fracture surface of bar sintered 4 hour in He at 1200<sup>0</sup> C.

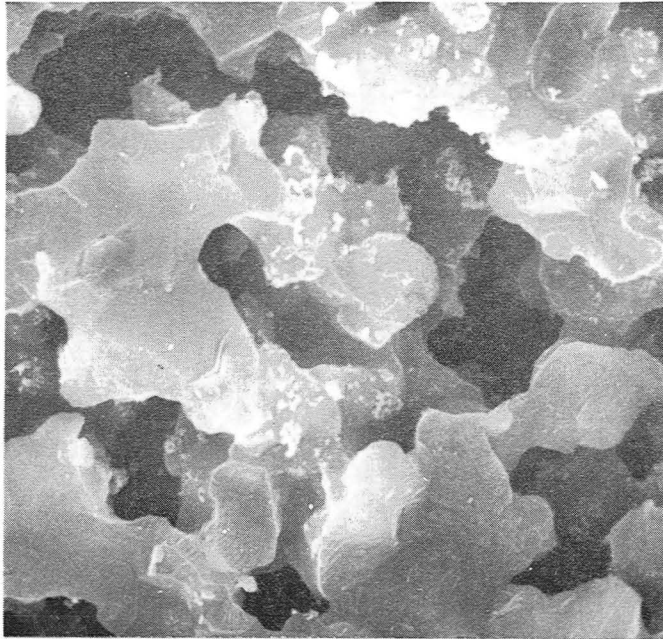


(a) NEAR SURFACE OF BAR.

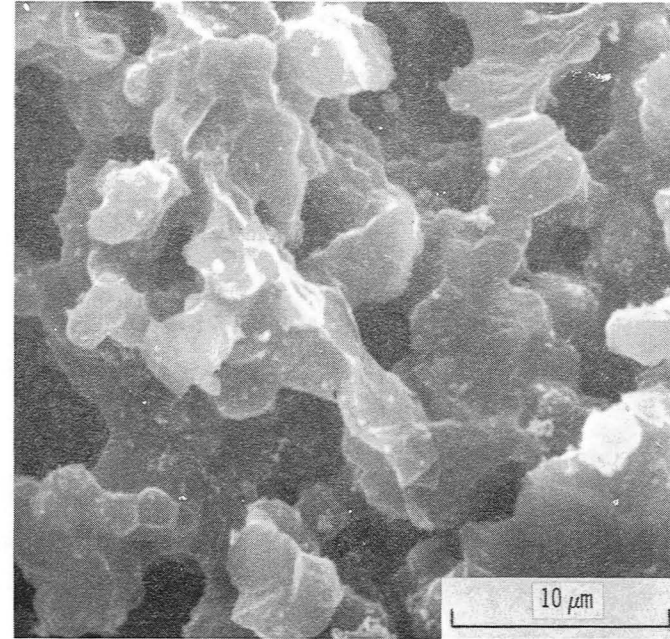


(b) INTERIOR OF BAR.

Figure 7. - SEM photographs of fracture surface of bar sintered with 0 hour hold at 1200° C.

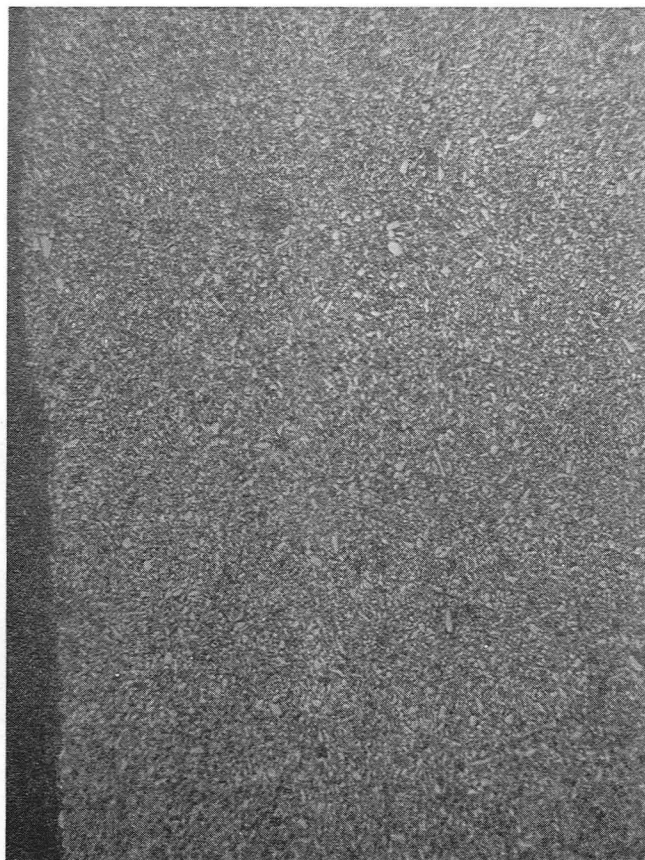


(a) TOP SURFACE OF BAR

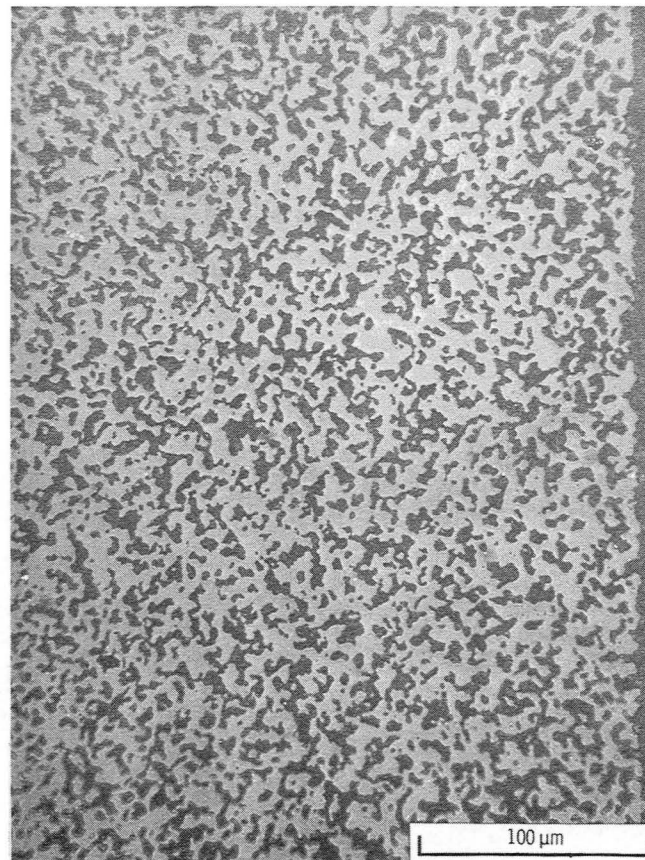


(b) INTERIOR AND BOTTOM

Figure 8. - SEM photographs of fracture surface of bar sintered 65 hours at 1200°C in He.



(a) 0 hour HOLD.



(b) 65 hour HOLD.

Figure 9. - Polished section of bars sintered at 1200°C in He.

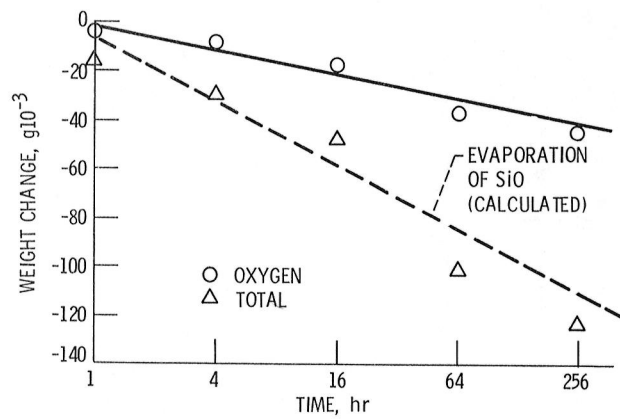


Figure 10. - Weight change during sintering of bars packed in  $\text{Si}_3\text{N}_4$  powder.

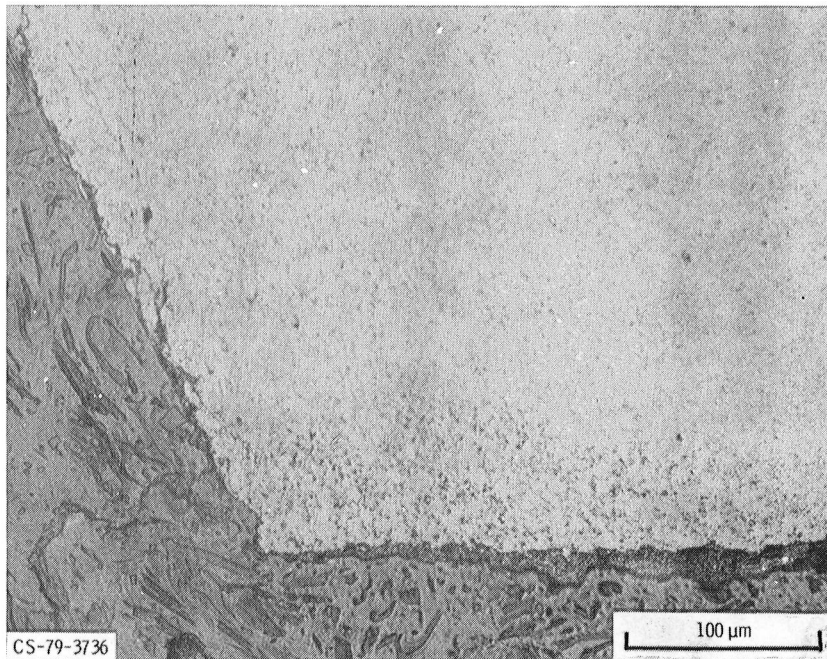


Figure 11. - Porous surface layer on bar nitrided exposed to gas flow.



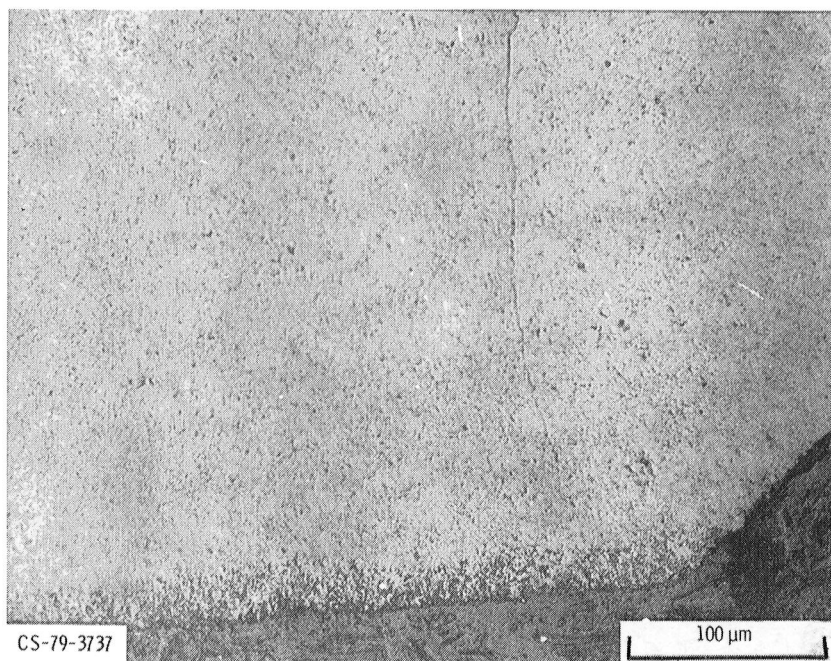


Figure 12. - Porous surface layer on bar nitrided packed in  $\text{Si}_3\text{N}_4$  powder.

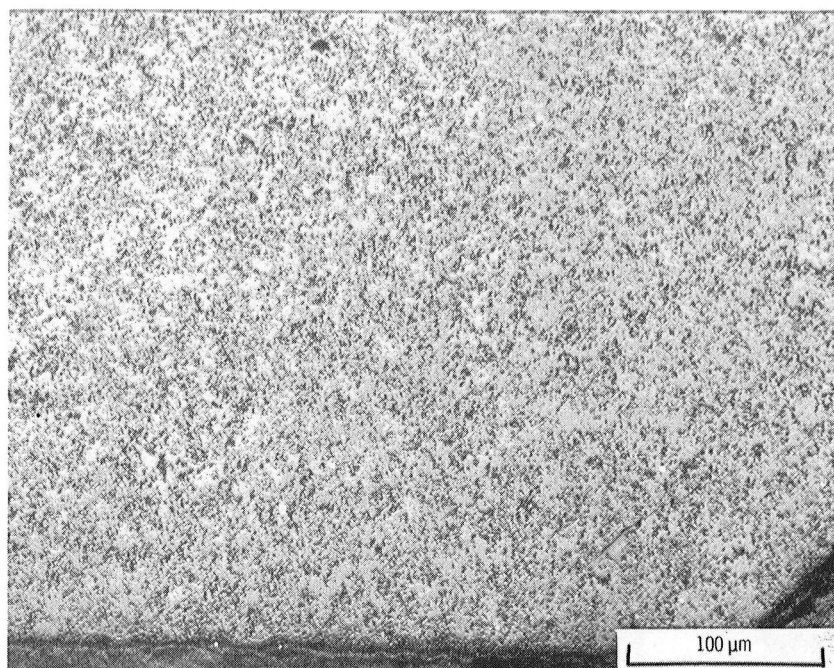


Figure 13. - Surface layer-free bar nitrided packed in Si powder.

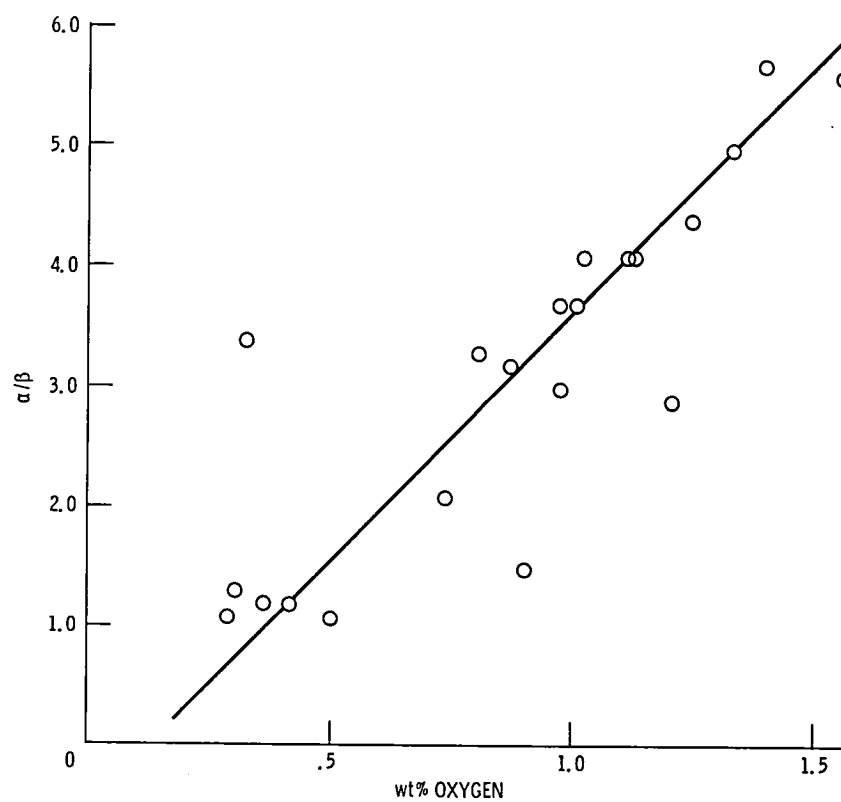
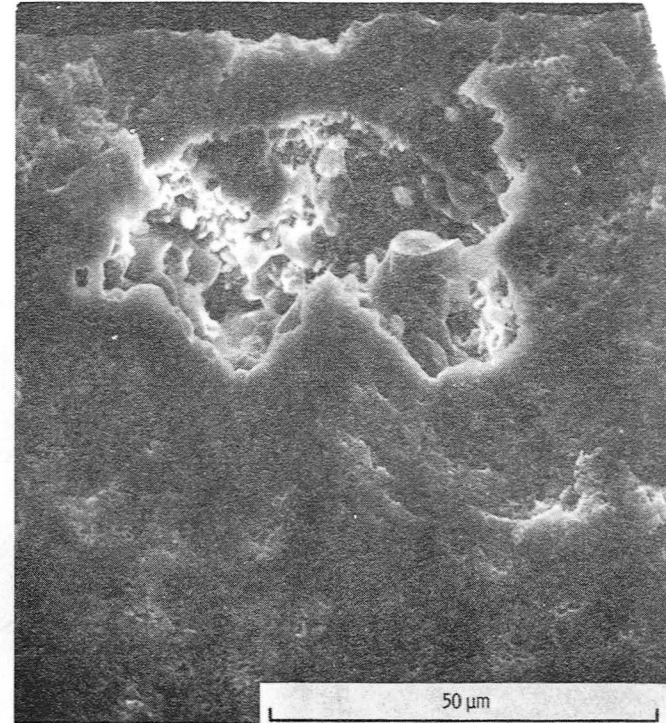


Figure 14. -  $\alpha/\beta$  Ratio vs oxygen content of nitrided bars.



(a) NEAR SURFACE.



(b) SURFACE.

Figure 15. - SEM photographs of fracture initiating flaws.





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16. Abstract  A study was undertaken to determine if the formation of the generally observed layer of large porosity adjacent to the as-nitride surfaces of RBSN could be prevented during processing. Isostatically pressed test bars were prepared from wet vibratory milled Si powder. Sintering and nitriding were each done under three different conditions: 1. bars directly exposed to the furnace atmosphere, 2. bars packed in Si powder, 3. bars packed in Si <sub>3</sub> N <sub>4</sub> powder. Packing the bars in either Si or Si <sub>3</sub> N <sub>4</sub> powder during sintering retarded formation of the layer of large porosity. Only packing the bars in Si prevented formation of the layer during nitridation. The strongest bars (316 MPa) were those sintered in Si and nitrided in Si <sub>3</sub> N <sub>4</sub> despite their having a layer of large surface porosity; failure initiated at very large pores and inclusions. The $\alpha/\beta$ ratio was found to be directly proportional to the oxygen content; a possible explanation for this relationship is discussed.					
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